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THE CONVERSION OF METHANE OVER SELECTED SOLID CATALYSTS

FINAL REPORT

BY

W. E. LEWIS

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Work on this project was conducted under the auspices of
Canada Centre for Mineral and Energy Technology,
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1. SUMMARY

With the decline of conventional crude oil reserves, alternate fuels and new processing routes to conventional transportation fuels will assume increasing importance. It is envisioned that gasoline will continue to be a major transportation fuel well into the next century. With Canada being resource rich in natural gas, there is a strong incentive to develop processing schemes for converting its major constituent, methane, into higher molecular weight hydrocarbons which are preferably in the gasoline boiling range. Methane can be incorporated into the gasoline pool via Fischer-Tropsch chemistry, converted to methanol for blending purposes or methanol may be further converted to gasoline via the Mobil MTG process. Each of these routes presents difficulties in terms of processing economics, by-product formation or material compatibility.

Direct conversion of methane to higher molecular weight hydrocarbons has received considerable attention from researchers but so far desirable product yields have been low. Approaches to methane oligomerization that have been documented are:

1. pyrolytic methane conversion,
2. oxidative coupling,
3. aluminosilicate catalysis, and
4. superacid process chemistry.

Microreactor scale studies have been carried out under the sponsorship of Energy, Mines and Resources Canada to evaluate some promising catalysts for the conversion of methane or methane/olefin mixtures to higher hydrocarbons. A number of catalysts were prepared by the metal salt impregnation procedure and corresponded to those described in journal publications or patent literature.

A nickel impregnated silica catalyst was evaluated for pyrolytic conversion of methane/propylene. Methane activation at 300°C and 500°C of a calcined material did not produce a catalyst with significant activity. Variations such as hydrogen reduction and methane reduction/activation of non-calcined material were not successful. Directionally, methane reduction/activation of non-calcined material at an intermediate temperature (e.g. 400-450°C) may produce a more active catalyst.

Both a tin/magnesium/sodium/silica catalyst and a manganese/magnesium/sodium/silica catalyst were evaluated for activity in the oxidative coupling reaction wherein the catalyst was alternately activated with oxygen (air) and then fed hydrocarbon feed. Neither catalyst possessed catalytic activity to oligomerize methane or methane/propylene at 670-680°C. Conceivably, higher reaction temperatures (800-900°C) could achieve catalytic activity.

Neither the gallium/zeolite catalyst nor the gallium/nickel/zeolite catalyst was sufficiently active to catalyze methane oligomerization when evaluated with a 4:1 feed of methane and nitrous oxide. Significantly, catalytic combustion occurred outside the methane flammability limits yielding oxides of carbon and water (see Appendix).

As none of the catalyst preparations explored produced any significant yields of C_2^+ hydrocarbons by oligomerization of methane or C_4^+ hydrocarbons by reaction of methane with propylene, it is not possible to conclude from this study which route possesses the greatest potential for methane conversion.

2. INTRODUCTION

2.1 General Background

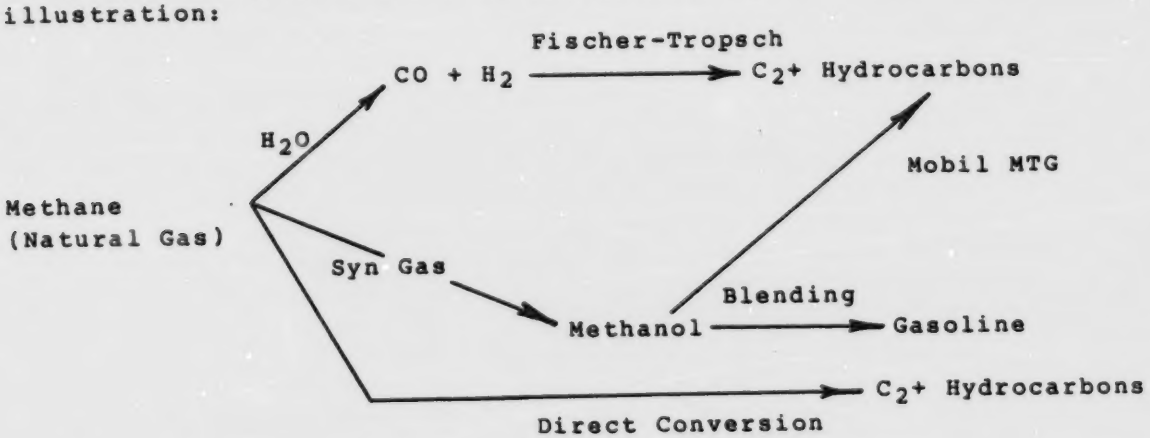
Despite significant gains in the utilization of alternate transportation fuels, gasoline will continue to play an important role as a major transportation fuel well into the next century. With the decline of conventional crude oil reserves in Canada increased dependence on foreign crude reserves seems inevitable. However, it is unlikely that the current situation of relatively low foreign crude prices will continue indefinitely. Rising prices will spur the development of more costly offshore crude oil production along with various in situ heavy oil and tar sands projects.

Canada is resource rich in natural gas which has significant potential for use as a transportation fuel. Direct use of compressed natural gas (CNG) will be limited by safety considerations while range limitations will probably restrict its widespread usage to commercial fleets. By comparison, gasoline is relatively safe to handle and transport either by pipeline, railway tank car or tank trucks and the distribution network is already well established.

Methane, the major constituent of natural gas, can be incorporated into the gasoline pool by three primary routes:

1. conversion to gasoline via synthesis gas
2. conversion to methanol intermediate
3. direct conversion to hydrocarbons in the gasoline boiling range

These processing routes may be represented by the following illustration:



Synthesis gas, a mixture of carbon monoxide and hydrogen, can be made by steam reforming of natural gas. Alternatively, residual oils, coal, or biomass may be the feedstock. Synthesis gas is subsequently converted to liquid fuels (Fischer-Tropsch chemistry) as in the present commercial operations of Sasol in South Africa (7.1). Unfortunately, this route is energy intensive due to the high cost of synthesis gas; the partial oxidation of the feed is highly endothermic.

Methanol is produced in the ICI process by steam reforming of natural gas followed by conversion over a catalyst containing oxides of zinc, copper and aluminum (7.1). Methanol can be used as a gasoline blending component to extend existing hydrocarbon blending pools. However, the quantity of methanol that can be blended with gasoline is limited to about 5 vol% by several factors:

1. significant increase in vapour pressure
2. need for cosolvent which is usually a higher alcohol to prevent methanol/water phase separation
3. methanol creates material compatibility problems in distribution and vehicle fuel systems.

The conversion of methanol to gasoline has received considerable attention with the Mobil MTG process recently achieving commercialization in New Zealand (7.1, 7.2). In the MTG process, methanol, produced by hydrolysis of natural gas, is converted to hydrocarbons in the gasoline boiling range in two stages, each employing fixed catalyst beds. First, the crude methanol is partially dehydrated over alumina to give an equilibrium mixture of methanol, dimethyl ether, and water. The effluent from the first stage reactor is then passed over a ZSM-5 synthetic zeolite catalyst to yield a mixture consisting mainly of gasoline fractions with dissolved carbon dioxide and some light (C_1-C_4) hydrocarbons.

More recently, in conjunction with West German researchers, Mobil has developed a fluid-bed process to convert methanol to gasoline (7.15). A 100 BPD demonstration plant demonstrated virtually complete conversion (99.9%) of methanol, with a gasoline yield better than 92%, including olefin recycling to product alkylates.

2.2 Direct Conversion of Methane

Conversion of methane to higher hydrocarbons without the isolation of intermediate products such as synthesis gas or methanol is of considerable importance and continues to be the subject of much research and development work. Haldar-Topsoe A/S in Denmark has developed the TIGAS (Topsoe Integrated Gasoline Synthesis) process (7.15). Although the TIGAS process produces gasoline from methane via methanol intermediate, the operation is integrated and operating pressures are chosen such that the three stages: namely synthesis gas production, methanol synthesis, and conversion of methanol to hydrocarbons, can be carried out at the same pressure. One of the main distinguishing features of the TIGAS process is that an oxygen stream must be supplied along with the feed reactants (methane or natural gas plus steam). Reaction products from the integrated process are LPG, water and gasoline.

A variety of alternate synthetic routes to produce heavier hydrocarbons directly from methane have been documented in the literature. These include:

1. pyrolytic methane conversion,
2. oxidative coupling,
3. aluminosilicate catalysis, and
4. superacid catalysis.

These approaches, while promising, have yet to be commercialized. Further discussion follows with emphasis on some of the more important studies.

2.2.1 Pyrolytic Methane Conversion

A silica supported nickel catalyst has been reported by Loffler et al. to catalyze the reaction between methane and olefins yielding a mixture of light hydrocarbons and C_5, C_6 liquids (7.3, 7.4). The reactions were carried out at moderate temperatures (330°C) and pressures (10 atm.). A typical feed of 94% methane/6% propylene yielded a product consisting of 53% C_1, C_2, 26% C_3H_8, 8.5%C_4 and 13% C_5, C_6 hydrocarbons. Active carbonaceous species formed on the catalyst surface by methane reduction at moderate temperatures were thought by the authors to enhance the formation of C_4 and heavier hydrocarbons (7.4). A search of the literature did not reveal other references pertaining to the pyrolytic conversion of methane solely over a supported nickel catalyst.

Alumina supported catalysts containing platinum, iridium, nickel, silver, or gold plus an oxide of chromium, molybdenum or tungsten in conjunction with an oxide of gallium indium or thallium have been claimed to pyrolytically convert methane to a mixture of products whose major constituents are ethylene and benzene (7.5). Typical reaction conditions were 620-870°C and atmospheric pressure. Product yields averaged about 4% each for ethylene and benzene. In an example from Reference 7.5, a methane feed was converted over a $MgAl_2O_4$ spinal blocked alumina supported catalyst containing 0.3% Pt, 5.0% Cr and 6.9% Ba at a temperature of 704°C to yield the following products:

Component	Mole %	% Methane Conversion to Product
CH_4	87.40	-
C_2H_4	6.29	8.0
C_2H_6	2.56	3.3
C_4H_8	0.02	-
C_6H_6	3.73	14.4

Tasks 2 and 3 of the present Contract (7.6) were designed to evaluate the potential for supported nickel catalysts to heterogeneously catalyze the pyrolytic conversion of methane/olefin feedstock to higher molecular weight hydrocarbons, preferably in the gasoline boiling range.

2.2.2 Oxidative Coupling

A large number of metal oxide catalysts have been reported to catalyze the coupling of light hydrocarbon molecules producing C_2+ hydrocarbons and water byproduct. These reactions are generally carried out in cyclical fashion wherein the catalyst is first activated with oxygen (air) at elevated temperatures followed by the passage of hydrocarbon feedstock. Keller and Bhasin reported methane conversion to C_2 hydrocarbons in the range 0-6% at temperatures of 500-1000°C with the most active catalysts containing oxides of tin, lead, antimony, bismuth, thallium, cadmium and manganese (7.7).

Jones et al. (7.8, 7.9) have developed catalysts consisting of a reducible metal oxide (e.g. Mn or Sn) plus an alkali metal (e.g.

Na, Li, or K) which may contain an alkaline earth metal (e.g. Mg or Ca) as well. In a later development of the invention (7.9), phosphorus may be added to enhance catalyst performance by extending its useful life. In an example from reference 7.9, a catalyst containing 10% Sn, 2% Na supported on SiO_2 gave 8.5% conversion of methane feed with a 73% selectivity to C_2+ hydrocarbons when tested at 900°C, 1 atm. and a gas hourly space velocity (GHSV) of 600 h^{-1}. Byproducts were oxides of carbon, coke and water. Product distribution for the C_2+ hydrocarbons was not given. Reference 7.8 illustrates the conversion of methane over a 5 wt% Sn/SiO_2 catalyst at 750°C and a GHSV (gas hourly space velocity) of 600 h^{-1} to yield the following results:

Run Time (min)	Conversion %	Selectivity, %					
		C_2H_4	C_2H_6	C_3	C_{4-7}	CO	CO_2
		Instantaneous Results					
0.5	7.23	9.9	14.6	0.4	0.4	9.2	65.4
1.0	1.25	18.2	35.6	0.7	1.0	2.3	42.2
2.0	0.43	30.7	67.6	1.3	-	0.2	-
		Cumulative Results					
15	0.54	24.7	40.8	0.9	2.5	13.0	17.8

From this example it can be seen that high feed conversion rates were favoured by short residence times while significant quantities of CO/CO_2 byproducts were produced. Product hydrocarbons were predominantly ethylene and ethane.

In Task 4 of the present Contract (6.6), two catalysts were prepared and evaluated for oxidative coupling of methane following procedures described in References 7.8 and 7.9. These catalysts were composed of a mixture of oxides of tin, magnesium and sodium supported on silica and a mixture of oxides of manganese, magnesium and sodium which was also silica supported.

2.2.3 Aluminosilicate Catalysis

Synthetically prepared aluminosilicates or zeolites are considered to have potential as catalysts for methane oligomerization due to the ability of their shape selective characteristics to favour specific reactions. For example, ZSM-5 zeolite has been reported

to convert C_2-C_4 paraffins and/or olefins to aromatics at temperatures in the range 100-700°C and pressures in the range 0-1000 psig (7.16).

Young claims a process wherein aliphatic hydrocarbons when mixed with an oxidizing agent and contacted with an aluminosilicate zeolite with a silica to alumina ratio greater than 12:1 yields a mixture of aromatic hydrocarbons having high octane values (7.13). The solid acidic catalyst is said to have Brönsted acid sites. Oxidizing agents may be nitrous oxide, sulfur trioxide, hydrogen peroxide, ozone, nitric oxide, and nitrogen oxyfluoride. In examples from Reference 7.13, the following results are achieved:

Catalyst	H-Zeolite	H-Zeolite
Hydrocarbon feed (GHSV)	CH_4 (120)	CH_4 (480)
Oxidant feed (GHSV)	N_2O (120)	N_2O (120)
Temperature, °C	450	450
Run Duration, minutes	315	150
Hydrocarbon feed conversion, %	39	11
Hydrocarbon yield, mole%	8.1	2.3
Product composition*, wt%		
C_2	5.9	2.7
C_3-C_5	3.3	1.0
C_6	3.0	3.8
C_7	9.1	13.8
C_8	25.2	29.9
C_9	16.0	10.8
C_{10}	6.3	9.0
C_{11}	16.1	16.2
C_{12}	13.8	12.4
C_{13}	1.3	0.4

* Methane free basis

The intent of Task 5 of the present Contract (7.6) was to prepare and evaluate two zeolite supported catalysts, one containing 3% gallium and the second containing 3% gallium plus 7.5% nickel. The feed consisted of a 4:1 mixture of methane and nitrous oxide.

2.2.4 Superacid Catalysis

Reaction of methane or methane/olefin mixtures in the presence of superacid catalysts has been reported by Olah (7.10, 7.11) and other researchers to yield higher molecular weight hydrocarbons ranging from ethylene/ethane through to oily polymers (7.12). Solid super acidic catalysts employed by Olah (7.10) included 10% tantalum pentafluoride supported on fluoridated alumina and 20% antimony pentafluoride deposited on a fluorinated graphite support. For example, a feed consisting of 90% methane/10% ethylene when contacted with the tantalum pentafluoride catalyst at 70°C in a continuous flow reactor gave a 38% conversion of ethylene. The methane-free product had the following composition:

Component	%
C_2H_6	13.2
C_3H_8	13.8
iC_4H_{10}	48.6
nC_4H_{10}	6.5
iC_5H_{12}	12.7
nC_5H_{12}	5.3

No experimental testing was done with superacids under the terms of the present contract. However, this area of study is being actively pursued by other researchers.

3. EXPERIMENTAL

3.1 Equipment

Catalyst evaluations including activation were carried out in a microreactor system illustrated schematically in Figure 1. Hydrocarbon feed gas blends, oxidants (air or nitrous oxide) and an inert purge gas (nitrogen) were provided by compressed gas cylinders. Following pressure reduction, feed gases were metered through precision rotameters (Rota Model LIVC.01) which were calibrated for the specific gas to be measured at the operating pressure and ambient temperature.

Blended gases passed downflow through a packed tubular reactor having an inside diameter of 9.4 mm and an overall length of 40.5 cm which was constructed from 1/2" O.D. X 0.065" wall type 316 stainless steel tubing. The reactor was surrounded by a brass heat sink to provide uniform heat distribution. Heat was supplied by a temperature controlled electric furnace (Hoskins Type FD 303A). Type K (chromel-alumel) thermocouples were inserted into thermowells machined into the brass heat sink blocks so that temperature measurements were made at approximately the 20% and 80% catalyst bed depth positions.

Powdered catalysts with particle sizes of 75-300 μm (Tasks 2, 3 and 5) or 100-500 μm (Task 4) were intimately mixed with equal volumetric proportions of 20-30 mesh borosilicate glass spheres. Typical loose packed catalyst volumes were 12-13 cm^3. Glass spheres were employed to disperse and support the powdered catalysts in order to minimize high reactor differential pressures developed when the finely divided catalysts were used alone. The catalyst/glass mixture was charged to the reactor tube and supported at either end by a combination of quartz wool and borosilicate glass spheres.

Upon exiting the reactor, the reaction products passed through a cooled gas/liquid separator designed to remove condensible hydrocarbons and water. In Task 2 runs, the separator vessel was a stainless steel cylinder refrigerated by a cooling water coil. An ice/water bath cooled glass cold trap was substituted for Task 5 runs. Non-condensible gases leaving the separator or cold trap passed through a back-pressure regulator set to maintain the run design pressure. Effluent gases then passed through a flow indicating rotameter and a gas meter (wet test type).

Provision was made for sampling of product gases in 125 mL glass orsats for gas chromatographic analyses. In Task 4 runs, the gas/liquid separator was replaced with a stainless steel tee fitted with a rubber septum. Gas samples were taken in 100 µL or 500 µL gas tight syringes for gas chromatographic analyses.

For experimental runs carried out at elevated pressures (Task 2), the contents of the separator vessel were transferred into a preweighed 10 cm^3 stainless steel sample cylinder at the end of the run. If a weight increase of the sample cylinder indicated the presence of liquids, then approximately 2 mL of solvent (n-hexadecane) were added to the cylinder which was then agitated. Upon release of pressurizing gas (helium), the liquids were recovered for gas chromatographic analyses. In Task 5 runs where the glass cold trap was used, the liquids produced were removed by pipetting techniques.

2.2 Data Evaluation

Feed gases charged to the microreactor were metered through calibrated precision rotameters. Mass flows of individual components were calculated from the gas composition and volumetric flowrates.

Reactor effluents were separated into condensible liquids and non-condensible gases. Separation was carried out in a water cooled (approx. 15°C) stainless steel separator (Figure 1) or in an ice bath cooled (0°C) glass cold trap (Task 5 runs). Liquids recovered at the end of a run were weighed. Liquid hydrocarbons, if present, would be characterized by gas chromatography. Total non-condensible gases were metered through a gas meter (wet test type) and were characterized by gas chromatography (Section 3.3.1). From gas composition and cumulative volume it was possible to calculate the mass of individual product components.

Mass balances, conversions and yields can be calculated from the above. However, since the experimental runs did not produce significant amounts of C_2+ hydrocarbons, these calculations were not necessary. A mass balance for Task 5, Run 2, is presented in Table 17 to illustrate that feed/product measurements were sufficiently accurate for this purpose.

3.3 Feed and Product Characterization

3.3.1 Gases

Cylinder gases used in the catalyst evaluations were obtained from Matheson Gas Products Canada with the exception of hydrogen (Task 2, Run 5) which was supplied by Canadian Liquid Air. Feed gases were characterized by gas chromatography (PCM 472-1 Appendix) and their compositions are given in Table 1. Hydrogen used in Task 2 had a manufacturer's reported minimum purity of 99.95%. Produced gases were sampled in 125 mL glass orsats (Tasks 2 and 5) or gas tight syringes and analyzed by gas chromatography (PCM 472-1).

3.3.2 Liquids

n-Hexadecane extracts from Task 2 runs were screened by GCD (gas chromatographic distillation) to determine the presence of other hydrocarbons.

Liquids obtained in Task 5 were tested for water solubility. As these tests were positive, no further characterization was done on this material.

3.4 Catalyst Preparation

All catalysts were prepared by impregnation of the support material with an aqueous solution of the metal salt (nitrate, acetate or tartrate).

Catalyst support materials were Houdry HSC 534 silica, Houdry HSC 114 γ-alumina and Union Carbide LZ-M-8 aluminosilicate (zeolite). Properties of these materials are given in Table 2. Union Carbide's Molecular Sieve Data sheet for LZ-M-8 zeolite is included in the Appendix. The Houdry supports were provided as extrusions (HSC 534) or spheres (HSC 114) while the LZ-M-8 zeolite was a powdered material. Following size reduction by grinding, the support material was oven dried at 110°C and then sieved through standard brass sieves. Particle size was 75-300 µm (Tasks 2, 3 and 5) or 100-500 µm (Task 4).

Appropriate weights of support material were weighed into a round bottom flask and then slurried with distilled water on a magnetic stirrer. Aqueous solutions of the metal salts were prepared to

known concentrations (typically 0.1 g/mL) and were then added in 10 mL aliquots to the stirred support such that the required ratios of metal to support were obtained (Table 3). Addition times were 2.0 h. Following salt solution addition, the mixtures were stirred an additional 2.0 h to ensure uniform salt distribution on the support material. Next the flask containing the catalyst slurry was transferred to a rotary evaporator apparatus. While rotating the suction was increased to about 29.5 torr and then the water bath temperature was slowly raised (final temp. 60°C) to remove water from the catalyst mixture. Evaporation times of about 2 h were necessary in order to prevent bumping of the catalyst mixture.

The dried catalyst was removed from the flask and any lumps were gently crushed. Catalyst powders were oven dried a minimum of 4 h at 105-110°C to remove excess moisture. Task 2, 3 and 5 catalysts were calcined by heating from 200 to 500°C and then maintaining this temperature for about 4 h. Task 4 catalysts were calcined in air at 700°C for 16 h.

3.5 Catalyst Activation/Preconditioning

All catalyst activations were carried out in situ in the micro-reactor by passing the activation/reduction gas downflow over the packed catalyst bed at an elevated temperature. Catalyst activation conditions are summarized in Table 4.

For Task 2 runs, attempts were made to maintain the gas hourly space velocities (GHSV) at 200 h^{-1}. However, some variation occurred due to coke formation on the catalyst creating an increasing reactor differential pressure. GHSV range was 179-210 h^{-1}.

Activation and similarly "run" conditions for Task 3 catalysts are not reported as no experimental evaluations were made with these three materials.

Task 4 catalysts were equilibrated by first passing the reactant gas (methane or methane/propylene blend) over the catalyst for 1.0 h and then regenerating for 1.0 h with air. Both of the above operations were carried out at "run" temperatures; i.e. approx. 670°C for Runs 3 and 6 and 500°C for Run 5. While the tin and manganese catalysts were intended to be evaluated at 700°C, average reactor temperatures of 670-680°C only were achieved representing

an upper temperature constraint for the microreactor heater. This temperature range was judged to be acceptable since the intent was to compare the performance of one catalyst against the other at the same operating conditions. Further, conversion of methane to C_2+ hydrocarbons over similar catalysts has been reported to occur over the range 500-1000°C (7.9).

Task 5 catalysts consisting of gallium and gallium/nickel on zeolite support were calcined at 500°C. The gallium/zeolite catalyst was evaluated without any preconditioning or activation step. Preconditioning of the gallium/nickel/zeolite catalyst was done with methane feed at 300°C for a period of 4.0 h.

3.6 Catalyst Characterization

The metal content of all catalysts prepared in Section 3.4 was determined by ICP-AA spectroscopy (Inductively coupled plasma-atomic absorption). All determinations on fresh catalysts were carried out on air calcined material. Spent catalysts were first fired overnight at 535°C in order to burn off coke. Samples of fresh or decoked catalyst were fused with lithium metaborate ($LiBO_2$) for 20 min at 900°C. After cooling, the fusion product was dissolved in 10% hydrochloric acid and then diluted to a standard volume with distilled water. The resultant solution was analyzed on a Perkin-Elmer Plasma II atomic absorption spectrometer and the metal content quantified by comparison with calibration curves prepared from standard solutions of metal salts. Metal contents of fresh and spent catalysts are given in Table 5.

Carbon contents of fresh activated (Task 2, Run 1) and spent catalysts (Tasks 2, 4, 5) are also presented in Table 5. Catalyst carbon contents were determined by combustion - infrared spectroscopy using a Leco Carbon Determinator - Model CR 12.

Task 2 catalyst assaying at 6.57% nickel was used in runs 1, 2, 5 and 6 while an independently prepared catalyst assaying at 7.02% nickel (calcined basis) was used in Run 4 to evaluate the potential for direct reduction/activation of the metal nitrate salt without prior calcination.

It was originally planned to prepare the zeolite supports used in Tasks 3 and 5 in the laboratory. As such, the Contract (7.6) required a measurement of crystallinity to establish that the material was not amorphous. As the zeolite employed was a commercially prepared material (Union Carbide LZ-M-8), agreement was obtained from the Scientific Authority to waive the crystallinity measurement.

4. RESULTS AND DISCUSSION

4.1 Task 2: Silica Supported Nickel Catalysts

A number of experimental microreactor runs were carried out to evaluate the ability of silica supported nickel catalysts to catalyze reaction of methane and propylene to form higher hydrocarbons (i.e. C_4+). While the activation of nickel catalysts through methane reduction has been reported (7.4), this reference was unavailable at the time the experimental work was carried out (Jan.-March, 1987). Therefore, a number of different activation and run conditions were explored in an attempt to produce a catalyst with appreciable activity. Specific run parameters are summarized in Table 6 for catalysts containing 7.5% (nominal) nickel on silica support.

Run 1 showed that activation at 488°C with methane gas for a 2.0 h period resulted in a catalyst having a carbon content of 5.57% (mass). In Run 2, catalyst activation was carried out as in Run 1. This catalyst was evaluated with 90% methane/10% propylene feed. Reactor effluent gases were collected over the course of the run and analyzed by gas chromatography (Table 7). No liquid products were produced. Examination of the effluent gas compositions indicated the following:

1. Propylene cracking followed by hydrogen addition produced ethylene and methane.

2. Concurrently olefin hydrogenation occurred to produce ethane and propane.

3. Hydrogen production was most probably due to hydrocarbon cracking with concurrent coke deposition yielding a spent catalyst with a carbon content of 8.12% (mass).

4. Catalyst activity with respect to hydrogenation declined throughout the run.

5. Minor amounts of C_4 olefins were formed.

Since methane activation of a calcined Ni/SiO_2 catalyst did not produce a material having significant activity, the direct reduction/activation of new material prepared by the impregnation

of silica with an aqueous nickel nitrate solution was examined. Freshly prepared catalyst having a nickel content of 7.02% (mass) (calcined basis) was preconditioned with methane gas in the micro-reactor (Table 6, Run 4). During the course of the activation nitrogen dioxide was evolved indicating the decomposition of the nitrate salt. Evaluation of this catalyst with 90% methane/10% propylene feed produced no liquid product. Reactor effluent gas compositions are given in Table 8. Performance of this catalyst was similar to that described in Run 2 but with somewhat higher activity.

Because of significant coke deposition in Runs 2 and 4, 8.12% and 9.06% (mass) respectively, reduction of calcined nickel catalyst with hydrogen was explored (Table 6, Run 5). This material was evaluated for activity with 90% methane/10% propylene feed. No liquid products were made in this run. Reactor effluent gas compositions are given in Table 9. The data indicate catalyst activity similar to Run 4 but with somewhat higher hydrogen content in the reactor effluent (approx. 0.5 mole%). The higher hydrogen content is thought to be due to coking reactions on the catalyst which had not been previously activated with methane. The spent catalyst had a significantly reduced carbon content at 3.71% (mass).

Run 6 had two objectives:

1. Reduced coking by carrying out the methane activation step at 300°C rather than 500°C. Activation time was extended from 2.0 to 4.0 h.

2. Run time with 90% methane/10% propylene feed was shortened from 4.0 to 1.0 h with more frequent sampling during the initial run period.

Reactor effluent gas samples were taken during both the activation and reaction periods. Activation gas analyses did not indicate any evolution of hydrogen during the first 2 h of the 4 h activation period. Consistent with this observation, spent catalyst at the end of the run contained only 0.05% (mass) carbon.

Analyses of reactor effluent gases taken during the reaction period (90% methane/10% propylene feed) are given in Table 10. Examination of these results indicates that the volume of gas retained in the reactor and associated tubing was sufficiently large to create

a lag in the emergence of the methane/propylene feed/product gases. Samples taken during the first 0.5 h reflected the composition of the methane activation gas. The sample taken after 1.0 h was approaching the composition of the methane/propylene feed. It was concluded that with the microreactor configuration used, run times greater than 1.0 h would be necessary for space velocities $<200\ h^{-1}$. However, the total absence of any C_4 or heavier hydrocarbons in the 40 and 60 min samples was interpreted as evidence of catalyst inactivity.

Activation of catalysts at 600°C was not attempted as specified in the Contract because of the significant coke production that occurred when methane activation was carried out at 500°C. Instead, a lower activation temperature (300°C) was examined (Run 6). All runs were conducted at "low" space velocities (GHSV = $200\ h^{-1}$) with the rationale that these low space velocities were most likely to favour the production of C_4+ hydrocarbons. As no significant formation of heavier hydrocarbons occurred in Runs 2-6, mass balance calculations and nitrogen/propylene feed reference runs became redundant.

Examination of the Loffler paper (7.4) which was received after the conclusion of the experimental work, indicates that a catalyst activation temperature of 410°C was used (pp 68-70). Furthermore, reduction may have been carried out directly on the nickel nitrate impregnated catalyst without air calcination. Comparison of reactor effluent gas compositions from Task 2, Run 2 and Run 4 indicates that higher concentrations of C_4+ hydrocarbons were found for Run 4 where the catalyst was in fact prepared without prior calcination. Following translation, recommendations for future studies on methane-activated nickel catalysts may become apparent.

4.2 Task 3: Alumina and Zeolite Supported Nickel Catalysts

The objective of Task 3 was to evaluate the activities of nickel catalysts on alumina and zeolite supports and higher concentrations of nickel on silica for comparison with the 7.5% nickel/silica catalyst used in Task 2. Three catalysts were prepared as described in Section 3.4 and were:

1. 7.5% Ni/alumina (HSC 114)
2. 7.5% Ni/Zeolite (LZ-M-8)
3. 20% Ni/silica (HSC 534)

Actual metal assays of the calcined catalysts are given in Table 5.

As no significant activity was demonstrated for the nickel/silica catalyst in Task 2, no experimental evaluations were made with the Task 3 catalysts. This course of action was discussed with and agreed upon by the Scientific Authority (7.14).

4.3 Task 4: Metal Oxide Catalysts

Two metal oxide catalysts were evaluated for their activity as oxidative coupling agents as described by Jones et al. (7.8, 7.9). Preparation and characterization of the catalysts is described in Sections 3.4 and 3.6. The catalysts were:

5% Sn/2% Mg/2% Na/silica (HSC 534), and
5% Mn/2% Mg/2% Na/silica (HSC 534).

Both catalysts were calcined in air at 700°C for 16 h.

Run parameters are summarized in Table 11. Catalysts were first preconditioned for 1.0 h with the feed gas followed by air regeneration for 1.0 h. Target temperatures for preconditioning and reaction were 700°C for Runs 3 and 6 but were limited to the range 668-683°C by the Hoskins furnace.

Run 3 evaluated the activity of the silica supported tin/magnesium/sodium oxide catalyst. Reactor effluent gas analyzes are presented in Table 12. The analyses show that fairly consistent effluent gas compositions were achieved for each of four successive one hour cycles. Only minor quantities (<0.1%) of ethylene and ethane were produced with no evidence of C_3+ hydrocarbon formation. Coproducts formed were carbon monoxide and carbon dioxide. Water, if present, would not have been detected by the gas chromatographic procedure employed.

In Run 6 the silica supported manganese/magnesium/sodium oxide catalyst was evaluated for activity with methane feed. Effluent gas compositions are given in Table 13. Analyses for the first two one-hour cycles are not available due to problems encountered with the gas syringe sample injection technique which highlighted the value of an on-line gas chromatograph in this type of study. Nevertheless, Cycle 3 and 4 analyses indicated low catalyst activity with only minor amounts of C_2 hydrocarbons being produced.

In Run 5 the silica supported tin/magnesium/sodium oxide catalyst was evaluated with a 90% methane/10% propylene (nominal composition) feed. As no optimum conditions were defined in Task 2, both the catalyst preconditioning and reaction run were carried out at 500°C, the maximum temperature employed for Task 2 catalyst evaluations. In selecting conditions for Run 5, a gas hourly space velocity (GHSV) of 600 h^{-1} was chosen so that product compositions could be compared against Runs 3 and 6 which also had a GHSV = 600 h^{-1}. Reactor effluent gas analyses for Run 5 are shown in Table 14. The analyses indicate low catalyst activity with only trace amounts of C_2 and C_4 hydrocarbons being formed. CO/CO_2 production was less than in Run 3 which was carried out with the same catalyst at a temperature of 669°C.

4.4 Task 5: Zeolite Supported Gallium/Nickel Catalysts

A gallium/aluminosilicate and a gallium/nickel aluminosilicate catalyst were tested for activity in conversion of methane to higher hydrocarbons in the presence of nitrous oxide oxidizing agent. The process of using a gallium loaded zeolite having Bronsted acid sites in the presence of an oxidizing agent has been reported to yield aromatic hydrocarbons (7.13). The preparation and characterization of catalysts used in Task 5 is described in Sections 3.4 and 3.6. The catalysts were:

3% Ga/Zeolite (LZ-M-8), and
3% Ga/7.5% Ni/Zeolite (LZ-M-8).

Both catalysts were calcined in air at 500°C.

Run parameters are summarized in Table 15. Run 2 evaluated the activity of the gallium/zeolite catalyst which received no preconditioning. The feed gas consisted of a 4:1 blend of methane and nitrous oxide with gas hourly space velocities of 480 h^{-1} and 120 h^{-1} respectively. The reaction temperature was 450°C. At the end of the run 2.49 g of liquid were recovered from the cold trap which was identified as water. Reactor effluent gas compositions are given in Table 16. Consistent with the water formation the gas samples contained the combustion products carbon monoxide, carbon dioxide and nitrogen. Nitrous oxide was completely consumed in the reaction. Minor amounts (<1%) of ethylene were detected in the effluent gas in the 2.0 h and 3.0 h samples. A mass balance for Run 2 is given in Table 17. A product:feed mass balance of 94.3% was obtained with losses accounted for as liquid (water) hold-up and gas metering error.

In Run 3, the gallium/nickel/zeolite catalyst was preconditioned with methane gas for 4.0 h @ 300°C, the conditions employed in Task 2, Run 6. Following this, the catalyst was evaluated with a 4:1 blend of methane and nitrous oxide with gas hourly space velocities of 480 h^{-1} and 120 h^{-1}, respectively; reaction temperature was 450°C. At the end of the run 1.91 g of of water were recovered from the cold trap. Reactor effluent gas analyses are shown in Table 18. As in Run 2, the effluent contained the products of combustion. Combustion proceeded further with the Ga/Ni/zeolite catalyst than with the Ga/zeolite catalyst as evidenced by the ratio of CO_2:CO and a spent catalyst carbon content of only 1.34% as opposed to 4.17% for Run 2. No C_2+ hydrocarbons were produced in Run 3.

5. CONCLUSIONS AND RECOMMENDATIONS

The metal salt impregnation procedure proved to be a satisfactory method to achieve the desired metal loadings on the support material. Metal loadings (calcined basis) fell in the range 85.5-94.3% of the target value with the exception of tin (77.2% and nickel (80.6%) for the 20% Ni/SiO_2 catalyst.

Small catalyst particle sizing presented operational difficulties with the microreactor due to high differential pressures. It was found that a mixture of the catalyst (75-300 μm) and borosilicate glass spheres (20-30 mesh) permitted the experimental runs to be conducted with differential pressures generally less than 20 psi. At the termination of each run, the catalyst bed was sieved through a 300 μm or 500 μm sieve to yield a catalyst recovery of approx. 90% based on charge weight. It is recommended that for future microreactor studies the catalyst should preferably be sized in the range 250-500 μm. The softening point of borosilicate glass (approx. 820°C) represents an upper temperature limit for the technique used. Alternatively, inert materials having a higher temperature resistance (e.g. quartz) could be used as dispersants.

From Task 2, Runs 1-6, some general conclusions can be made with respect to methane activated silica supported nickel catalysts:

1. Activation temperatures in excess of 300°C are necessary for deposition of carbonaceous species on the Ni/SiO_2 catalyst surface.

2. Pyrolytic decomposition of hydrocarbons occurred at 480°C depositing carbon on the catalyst and liberated hydrogen.

3. The hydrogen produced was consumed by olefins yielding saturates. Hydrogenation activity of the catalyst decreased with coke make.

4. The catalysts prepared by nickel nitrate impregnation of silica, calcination in air, and methane activation at 500°C did not possess significant activity at the reaction conditions tested (300°C, 150 psia, GHSV=200 h^{-1}) to catalyze methane/propylene reaction.

The methane activation of non-calcined nickel nitrate impregnated silica should be investigated at 400-450°C. Following translation

of Reference 7.4, additional recommendations for future studies may become apparent.

Neither the $Sn/Mg/Na/SiO_2$ catalyst nor the $Mn/Mg/Na/SiO_2$ catalyst prepared in Task 4 runs possessed catalytic activity to oligomerize methane under the reaction conditions (670-680°C, 1 atm., GHSV=600 h^{-1}). Evaluation of the tin catalyst with 90% methane/10% propylene feed yielded only trace quantities (<0.1%) of C_2 and C_4 hydrocarbons. Conceivably, higher reaction temperatures (800-900°C) could result in improved catalyst performance.

With a 4:1 feed mixture of methane and nitrous oxide, the gallium/ LZ-M-8 zeolite catalyst produced only low concentrations (<1%) of ethylene. Significantly, combustion occurred outside the methane flammability limits causing total extinction of nitrous oxide. This observation underscores inherent difficulties in this route in that reactor cooling would be necessary to prevent thermal excursions. Methane activation of the gallium/nickel/ LZ-M-8 zeolite catalyst at 300°C did not produce a catalyst with significant activity for methane oligomerization with methane/ nitrous oxide feed. Even if active carbonaceous sites could be established by activation at higher temperatures, it is probable that they would be consumed by subsequent combustion reactions.

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FIGURE 1 METHANE CONVERSION MICROREACTOR

TABLE 1

FEED GAS COMPOSITIONS

Composition (mole %)	Methane	90% Methane/ 10% Propylene	Nitrous Oxide	80% Methane/ 20% Nitrous Oxide*
Methane	99.76	89.24	0.04	80.33
Ethylene	0.00	0.00		
Ethane	0.16	0.15		0.15
Propylene	0.03	10.50		
Propane	0.03	0.07		
n-Butane		0.01		
C_6^+		0.01		
Carbon dioxide	0.02	0.02		
Nitrogen				0.54
Nitrous Oxide			99.96	18.98

*Task 5 - Proportional flow (rotameter) blend.

TABLE 2

CATALYST SUPPORT PROPERTIES

	Houdry HSC 534	Houdry HSC 114	Union Carbide LZ-M-8
Composition, mass %			
SiO_2	99.5 min	--	86.1
γ-Al_2O_3	--	99.5 min	8.6
SiO_2/Al_2O_3, molar ratio	--	--	17.0
Surface Area, m^2/g (nitrogen)	190	250	480
Pore Volume, cm^3/g			
(nitrogen)	0.8	0.3	--
(mercury)	1.1	--	--

Properties shown are manufacturers' typical values.

TABLE 3

CATALYST REAGENTS

Catalyst	Metal Salt	Wt. Salt g	Wt. Metal g	Wt. Support g
Task 2				
7.5% Ni/SiO_2	$Ni(NO_3)_2 \cdot 6H_2O$	18.58	3.75	46.25
Task 3				
7.5% Ni/Al_2O_3	$Ni(NO_3)_2 \cdot 6H_2O$	18.58	3.75	46.25
7.5% Ni/LZ-M-8	$Ni(NO_3)_2 \cdot 6H_2O$	18.58	3.75	46.25
20% Ni/SiO_2	$Ni(NO_3)_2 \cdot 6H_2O$	49.55	10.00	40.00
Task 4				
5% Sn/2% Mg/2% Na/SiO_2	$SnC_4H_4O_6$*	5.62	2.50	45.50
	$Mg(C_2H_3O_2)_2 \cdot 4H_2O$	8.82	1.00	
	$NaC_2H_3O_2 \cdot 3H_2O$	5.92	1.00	
5% Mn/2% Mg/2% Na/SiO_2	$Mn(C_2H_3O_2)_2 \cdot 4H_2O$	11.15	2.50	45.50
	$Mg(C_2H_3O_2)_2 \cdot 4H_2O$	8.82	1.00	
	$NaC_2H_3O_2 \cdot 3H_2O$	5.92	1.00	
Task 5				
3% Ga/LZ-M-8	$Ga(NO_3)_3 \cdot 8H_2O$	8.60	1.50	48.50
3% Ga/7.5% Ni/LZ-M-8	$Ga(NO_3)_3 \cdot 8H_2O$	8.60	1.50	44.75
	$Ni(NO_3)_2 \cdot 6H_2O$	18.58	3.75	

* Dissolved in 10% HCl

TABLE 4

CATALYST ACTIVATION/PRECONDITIONING PARAMETERS

Task No.	Run No.	Catalyst Type	Preconditioning/Activation Conditions				
			Feed Gas	Temp °C	Press psia	Time h	GHSV h^{-1}
2	1	Ni/SiO_2[1]	CH_4	488	14.7	2.0	200
2	2	Ni/SiO_2	CH_4	485	14.7	2.0	180
2	4	Ni/SiO_2	CH_4	490	14.7	2.0	179
2	5	Ni/SiO_2	H_2	499	14.7	2.0	210
2	6	Ni/SiO_2	CH_4	300	14.7	4.0	195
4	3	$Sn/Mg/Na/SiO_2$[2]	CH_4	668	14.7	1.0	600
			Air	668	14.7	1.0	600
4	5	$Sn/Mg/Na/SiO_2$[2]	90% CH_4/ 10% C_3H_6	500	14.7	1.0	600
			Air	499	14.7	1.0	600
4	6	$Mn/Mg/Na/SiO_2$[3]	CH_4	673	14.7	1.0	600
			Air	683	14.7	1.0	600

NOTES

1 Run 1,2,5,6 6.57% Ni/SiO_2, calcined at 500°C
Run 4 7.02% Ni/SiO_2, non-calcined

2 3.86% Sn/1.84% Mg/1.80% Na, calcined at 700°C

3 4.40% Mn/1.83% Mg/1.71% Na, calcined at 700°C

TABLE 5

CATALYST CHARACTERIZATION

Task No.	Run No.	Catalyst Description	Metal Assay[1] mass %	Carbon mass %
2		7.5% Ni/SiO_2[2] (Fresh)	Ni 6.57	--
2	1	7.5% Ni/SiO_2 (Activated)	Ni 6.50	5.57
2	2	7.5% Ni/SiO_2 (Spent)	Ni 6.50	8.12
2	4	7.5% Ni/SiO_2 (Fresh)	Ni 7.02	--
2	4	7.5% Ni/SiO_2 (Spent)	Ni 6.45	9.06
2	5	7.5% Ni/SiO_2 (Spent)	Ni 6.51	3.86
2	6	7.5% Ni/SiO_2 (Spent)	Ni 6.42	0.05
3		7.5% Ni/Al_2O_3[3] (Fresh)	Ni 6.86	--
3		7.5% Ni/Zeolite[4] (Fresh)	Ni 6.96	--
3		20% Ni/SiO_2 (Fresh)	Ni 16.12	--
4		5% Sn/2% Mg/2% Na/SiO_2 (Fresh)	Sn 3.86/Mg 1.84/Na 1.80	--
4	3	5% Sn/2% Mg/2% Na/SiO_2 (Spent)	Sn 2.91/Mg 1.56/Na 1.51	0.03
4	5	5% Sn/2% Mg/2% Na/SiO_2 (Spent)	Sn 3.73/Mg 1.90/Na 1.70	<0.01
4		5% Mn/2% Mg/2% Na/SiO_2 (Fresh)	Mn 4.40/Mg 1.83/Na 1.71	--
4	6	5% Mn/2% Mg/2% Na/SiO_2 (Spent)	Mn 4.58/Mg 1.96/Na 2.00	<0.01
5		3% Ga/Zeolite (Fresh	Ga 2.83	--
5	2	3% Ga/Zeolite (Spent)	Ga 2.63	4.17
5		3% Ga/7.5% Ni/Zeolite (Fresh)	Ga 2.76/Ni 7.35	--
5	3	3% Ga/7.5% Ni/Zeolite (Spent)	Ga 2.72/Ni 6.95	1.34

NOTES:
1 Metal assays on calcined catalysts
2 SiO_2 - Houdry HSC 534
3 Al_2O_3 - Houdry HSC 114
4 Zeolite - Union Carbide LZ-M-8

TABLE 6

TASK 2: CATALYST EVALUATION RUNS

Run No.	Catalyst Type	Catalyst Wt. g	Reduction/Activation Conditions Feed	Temp °C	Press psia	Time h	GHSV h^{-1}	Run Conditions Feed	Temp °C	Press psia	Time h	GHSV h^{-1}
1	6.57% Ni/SiO_2[1]	4.70	CH_4	488	14.7	2.0	200					
2	6.57% Ni/SiO_2	4.13	CH_4	485	14.7	2.0	180	CH_4/C_3H_6[3]	287	150	4.5	188
4	7.02% Ni/SiO_2[2]	5.75	CH_4	490	14.7	2.0	179	CH_4/C_3H_6	300	150	5.0	206
5	6.57% Ni/SiO_2	4.15	H_2	499	14.7	2.0	210	CH_4/C_3H_6	299	150	4.0	179
6	6.57% Ni/SiO_2	4.71	CH_4	300	14.7	4.0	195	CH_4/C_3H_6	300	150	1.0	199

GHSV: Gas hourly space velocity (vol. feed gas at STP/vol catalyst)

1 6.57% mass Ni/SiO_2 - dried 4 h at 105°C, calcined at 500°C

2 7.02% mass Ni/SiO_2 - dried 4 h at 105°C, non-calcined

3 CH_4/C_3H_6 - 90/10%

TABLE 7

TASK 2 - RUN 2: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent			
		1.5 h	2.5 h	3.5 h	4.5 h
Methane	89.24	89.94	89.60	89.52	89.49
Ethylene	-	0.05	0.05	0.05	0.02
Ethane	0.15	0.26	0.21	0.20	0.20
Propylene	10.50	8.42	9.02	9.25	9.39
Propane	0.07	1.17	0.83	0.69	0.62
Butene-1	-	0.03	0.03	0.02	0.02
iso-Butene	-	0.01	0.01	0.01	0.01
trans-2-Butene	-	0.03	0.01	0.01	0.01
cis-2-Butene	-	0.02	0.01	0.01	0.01
iso-Butane	-	0.01	-	0.01	-
n-Butane	0.01	0.01	0.01	0.01	0.01
iso-Pentane	-	-	0.01	-	-
n-Pentane	-	-	0.02	-	-
C_6+, C_5-S, cP[2]	0.01	0.03	0.02	0.02	0.02
Hydrogen	-	-	0.16	0.18	0.18
Carbon monoxide	-	-	-	-	-
Carbon dioxide	0.02	0.02	0.01	0.02	0.02

1 Nitrogen and oxygen free basis.

2 C_6+ = hexanes plus, C_5-S = C_5 olefins, cP = cyclopentane

Analytical accuracy $\pm$ 0.01%

TABLE 8

TASK 2 - RUN 4: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent		
		1 h	3 h	5 h
Methane	89.24	90.65	90.00	90.15
Ethylene	-	0.05	0.05	0.05
Ethane	0.15	0.41	0.33	0.26
Propylene	10.50	6.33	8.13	8.37
Propane	0.07	2.29	1.32	1.08
Butene-1	-	0.04	0.03	0.03
iso-Butene	-	0.03	0.02	0.01
trans-2-Butene	-	0.06	0.03	0.02
cis-2-Butene	-	0.05	0.03	0.01
iso-Butane	-	-	-	-
n-Butane	0.01	0.03	0.01	-
iso-Pentane	-	-	-	-
n-Pentane	-	-	-	-
C_6^+, C_5^-S, cP	0.01	0.06	0.04	0.04
Hydrogen	-	-	-	-
Carbon monoxide	-	-	-	-
Carbon dioxide	0.02	-	0.01	-

1 Nitrogen and oxygen free basis.

TABLE 9

TASK 2 - RUN 5: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent		
		1 h	2 h	4 h
Methane	89.24	90.20	90.11	89.80
Ethylene	-	0.04	0.05	0.16
Ethane	0.15	0.46	0.38	0.25
Propylene	10.50	5.60	7.00	7.97
Propane	0.07	2.56	1.78	1.29
Butene-1	-	0.04	0.04	0.04
iso-Butene	-	0.03	0.03	0.02
trans-2-Butene	-	0.06	0.04	0.03
cis-2-Butene	-	0.05	0.03	0.02
iso-Butane	-	0.01	-	-
n-Butane	0.01	0.04	0.02	0.01
iso-Pentane	-	0.01	-	-
n-Pentane	-	-	-	-
C_6+, C_5-S, cP	0.01	0.05	0.05	0.04
Hydrogen	-	0.53	0.46	0.37
Carbon monoxide	-	-	-	-
Carbon dioxide	0.02	0.02	0.01	-

1 Nitrogen and oxygen free basis.

TABLE 10

TASK 2 - RUN 6: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed		Effluent				
	Activation	Run	5 min	10 min	20 min	40 min	60 min
Methane	99.76	89.24	99.80	99.80	99.79	96.97	91.22
Ethylene	-	-	-	-	0.02	-	-
Ethane	0.16	0.15	0.20	0.17	0.15	0.15	0.16
Propylene	0.03	10.50	-	-	0.03	2.40	8.31
Propane	0.03	0.07	-	0.03	0.01	0.03	0.06
Butene-1	-	-	-	-	-	-	-
iso-Butene	-	-	-	-	-	-	-
trans-2-Butene	-	-	-	-	-	-	-
cis-2-Butene	-	-	-	-	-	-	-
iso-Butane	-	-	-	-	-	-	-
n-Butane	-	0.01	-	-	-	-	-
iso-Pentane	-	-	-	-	-	-	-
n-Pentane	-	-	-	-	-	-	-
C_6+, C_5^{-S}, cP	-	0.01	-	-	-	-	-
Hydrogen	-	-	-	-	-	-	-
Carbon monoxide	-	-	-	-	-	0.45	0.22
Carbon dioxide	0.02	0.02	-	-	-	-	0.03

[1] Nitrogen and oxygen free basis.

See Section 4.1 for discussion of the significance of these gas compositions.

TABLE 11

TASK 4: CATALYST EVALUATION RUNS

Run No.	Catalyst Type	Catalyst wt. g	Preconditioning Feed	Temp °C	Press psia	Time h	GHSV** h^{-1}	Run Conditions Feed	Temp °C	Press psia	Cycles*	GHSV** h^{-1}
3	$Sn/Mg/Na/SiO_2$	5.27	CH_4	668	14.7	1.0	600	CH_4	669	14.7	4	600
			Air	668	14.7	1.0	600					
5	$Sn/Mg/Na/SiO_2$	5.24	90% CH_4/ 10% C_3H_6	500	14.7	1.0	600	90% CH_4/ 10% C_3H_6	500	14.7	4	600
			Air	499	14.7	1.0	600					
6	$Mn/Mg/Na/SiO_2$	6.80	CH_4	673	14.7	1.0	600	CH_4	682	14.7	4	600
			Air	683	14.7	1.0	600					

* Cycle:

CH_4 Feed	2 min
N_2 Purge	15 min
Air Regeneration	30 min
N_2 Purge	15 min

**GHSV: Gas hourly space velocity (vol feed gas at STP/vol catalyst)

TABLE 12

TASK 4 - RUN 3: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent[2]			
		Cycle 1	Cycle 2	Cycle 3	Cycle 4
Methane	99.76	98.69	98.42	98.38	98.55
Ethylene	-	0.07	0.09	0.06	0.08
Ethane	0.16	0.22	0.22	0.20	0.25
Propylene	0.03	-	-	-	-
Propane	0.03	-	-	-	-
Butene-1	-	-	-	-	-
iso-Butene	-	-	-	-	-
trans-2-Butene	-	-	-	-	-
cis-2-Butene	-	-	-	-	-
iso-Butane	-	-	-	-	-
n-Butane	-	-	-	-	-
iso-Pentane	-	-	-	-	-
n-Pentane	-	-	-	-	-
C_6^+, C_5^-S, cP	-	-	-	-	-
Hydrogen	-	-	-	-	-
Carbon monoxide	-	0.68	0.88	1.03	0.79
Carbon dioxide	0.02	0.34	0.39	0.33	0.33

1 Nitrogen and oxygen free basis.

2 Samples taken at end of 2 min hydrocarbon feed period for each cycle.

TABLE 13

TASK 4 - RUN 6: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent[2]	
		Cycle 3	Cycle 4
Methane	99.76	99.45	99.71
Ethylene	-	0.18	-
Ethane	0.16	0.31	0.29
Propylene	0.03	0.01	-
Propane	-	0.02	-
Butene-1	-	-	-
iso-Butene	-	-	-
trans-2-Butene	-	-	-
cis-2-Butene	-	-	-
iso-Butane	-	-	-
n-Butane	-	-	-
iso-Pentane	-	-	-
n-Pentane	-	-	-
C_6+, C_5^{-S}, cP	-	-	-
Hydrogen	-	-	-
Carbon monoxide	-	-	-
Carbon dioxide	0.02	0.03	-

1 Nitrogen and oxygen free basis

2 Cycle 1 and 2 samples - analysis not available
Samples taken at end of 2 min hydrocarbon feed period for each cycle

TABLE 14

TASK 4 - RUN 5: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent[2]	
		Cycle 1	Cycle 2
Methane	89.24	89.15	89.16
Ethylene	-	0.08	0.07
Ethane	0.15	0.22	0.17
Propylene	10.50	10.42	10.45
Propane	0.07	0.08	0.07
Butene-1	-	-	-
iso-Butene	-	-	0.05
trans-2-Butene	-	-	-
cis-2-Butene	-	-	-
iso-Butane	-	-	-
n-Butane	0.01	-	-
1,3-Butadiene	-	0.01	-
iso-Pentane	-	-	-
n-Pentane	-	-	-
C_6+, C_5-S, cP	-	-	-
Hydrogen	-	-	-
Carbon monoxide	-	-	-
Carbon dioxide	0.02	0.04	0.03

1 Nitrogen and oxygen free basis

2 Cycle 3 and 4 samples - analysis not available, samples taken at end of 2 min hydrocarbon feed period for each cycle

TABLE 15

TASK 5: CATALYST EVALUATION RUNS

Run No.	Catalyst Type	Wt. g	Preconditioning Feed	GHSV* h^{-1}	Temp °C	Press psia	Time h	Run Conditions Feed	GHSV* h^{-1}	Temp °C	Press psia	Time h
2	2.83% Ga/Zeolite	5.61						CH_4 N_2O	480 120	450	14.7	4.0
3	2.76% GA/7.35% Ni/ Zeolite	7.08	CH_4	392	300	14.7	4.0	CH_4 N_2O	480 120	450	14.7	4.0

* GHSV: Gas hourly space velocity (vol feed gas at STP/vol Catalyst)

TABLE 16

TASK 5 - RUN 2: REACTOR GAS COMPOSITIONS

Composition[1] mole %	Feed	Effluent[2] 0.5 h	1.0 h	2.0 h	3.0 h
Methane	80.33	74.35	74.57	72.98	73.69
Ethylene	-	0.04	-	0.42	0.57
Ethane	0.15	0.13	0.14	0.15	0.14
Propylene	-	-	-	-	-
Propane	-	-	-	-	-
Butene-1	-	-	-	-	-
iso-Butene	-	-	-	-	-
trans-2-Butene	-	-	-	-	-
cis-2-Butene	-	-	-	-	-
iso-Butane	-	-	-	-	-
n-Butane	-	-	-	-	-
iso-Pentane	-	-	-	-	-
n-Pentane	-	-	-	-	-
C_6^+, C_5^{-S}, cP	-	-	-	-	-
Hydrogen	-	-	-	-	-
Carbon monoxide	-	2.74	3.00	3.27	3.09
Carbon dioxide	-	1.58	1.83	2.22	2.20
Nitrous oxide	18.98	-	-	-	-
Nitrogen	0.54	21.16	20.46	20.96	20.31

[1] Oxygen free basis.

[2] Water (cumulative) = 2.49 g

TABLE 17

TASK 5 - RUN 2: MASS BALANCE

Component	Feed				Product (Run Average)			
	Mol. Wt.	Mol.%	Mass %	Wt. g	Mol. %	Mass %	Wt. g	
Methane	16.032	80.33	60.09	18.30	73.90	60.82	15.81	
Ethylene	28.032	-	-	-	0.26	0.37	0.10	
Ethane	30.048	0.15	0.21	0.06	0.14	0.22	0.06	
Carbon Monoxide	28.000	-	-	-	3.03	4.36	1.13	26.00
Carbon Dioxide	44.000	-	-	-	1.96	4.43	1.15	
Nitrous Oxide	44.020	18.98	38.99	11.87	-	-	-	
Nitrogen	28.020	0.54	0.71	0.22	20.72	29.80	7.75	
Water	18.016	-	-	-	-	-	2.49	
Carbon on Catalyst	12.000			-			0.23	
				30.45			28.72	

Feed

Example: CH_4: (16.032 g/mole) (130 cc/min) (245 min) (1 L/1000 cc) (1 mole/22.414 L) (0.8033) = 18.30 g

Product

(27.18 L) (1 mole/22.414 L) (21.44* g/mole) = 26.00 g

* Weighted average molecular weight

Mass Balance

$$\frac{\text{Product}}{\text{Feed}} \times 100 = \frac{28.72\ \text{g}}{30.45\ \text{g}} \times 100 = 94.3\%$$

TABLE 18

TASK 5 - RUN 3: REACTOR GAS COMPOSITIONS

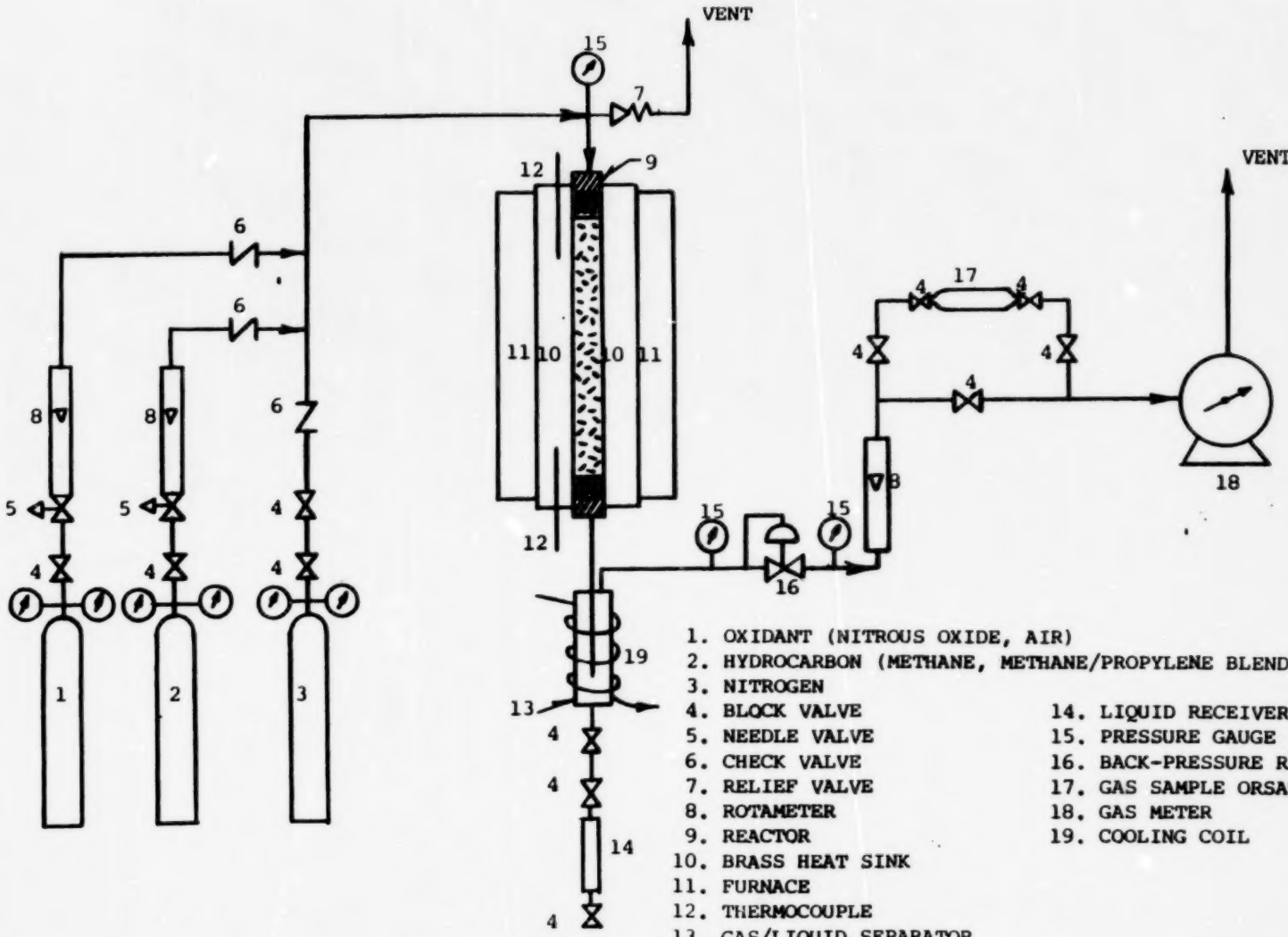
Composition[1] mole %	Feed	Effluent[2]		
		1 h	2 h	2.5 h
Methane	80.33	65.70	62.05	61.12
Ethylene	-	-	-	-
Ethane	0.15	-	-	0.04
Propylene	-	-	-	-
Propane	-	-	-	-
Butene-1	-	-	-	-
iso-Butene	-	-	-	-
trans-2-Butene	-	-	-	-
cis-2-Butene	-	-	-	-
iso-Butane	-	-	-	-
n-Butane	-	-	-	-
iso-Pentane	-	-	-	-
n-Pentane	-	-	-	-
C_6^+, C_5^{-S}, cP	-	-	-	-
Hydrogen	-	-	-	-
Carbon monoxide	-	1.79	1.85	1.42
Carbon dioxide	-	7.31	8.26	8.37
Nitrous oxide	18.98	-	-	-
Nitrogen	0.54	25.20	27.84	29.05

1 Oxygen free basis.

2 Water (cumulative) = 1.91 g

FIGURE 1

METHANE CONVERSION MICROREACTOR



1. OXIDANT (NITROUS OXIDE, AIR)
2. HYDROCARBON (METHANE, METHANE/PROPYLENE BLEND)
3. NITROGEN
4. BLOCK VALVE
5. NEEDLE VALVE
6. CHECK VALVE
7. RELIEF VALVE
8. ROTAMETER
9. REACTOR
10. BRASS HEAT SINK
11. FURNACE
12. THERMOCOUPLE
13. GAS/LIQUID SEPARATOR
14. LIQUID RECEIVER
15. PRESSURE GAUGE
16. BACK-PRESSURE REGULATOR
17. GAS SAMPLE ORSAT
18. GAS METER
19. COOLING COIL

A P P E N D I X

CONTENTS

1. PCM 472-1, Determination of C_2-C_5, C_6+ Hydrocarbons, H_2, O_2, N_2, CO, CO_2 and H_2S in Petroleum Gases (Gas Chromatography).

2. Union Carbide Molecular Sieve Catalyst Data.

3. Task 5 - Flammability Calculations

DETERMINATION OF C_1-C_5, C_6+ HYDROCARBONS, H_2, O_2, N_2, CO, CO_2 AND H_2S IN PETROLEUM GASES

(GAS CHROMATOGRAPHY)

1. OUTLINE OF METHOD

Gas samples are analyzed on a Carle Refinery Gas Analyzer. The instrument is a "packaged" gas chromatograph with a thermal conductivity detector, three multipurpose switching valves and a palladium hydrogen transfer system. All twenty-three components are determined from a single analysis and are resolved on a combination of five chromatographic columns. Quantitation is achieved by internal normalization of response corrected peak areas.

2. SCOPE

PCM 472 determines H_2, O_2, CO, CO_2, light paraffins (C_1-C_5), light olefins (C_2-C_4), acetylene, propadiene, 1,3-butadiene and H_2S in gases that have low C_6+ content. The C_6+ paraffins, C_5+ olefins and cyclopentane are eluted as a composite backflush peak at the beginning of the analysis. The detection limit of individual components is 0.005 mole %. Components other than those listed above, if present, will interfere with the analysis.

3. APPARATUS

3.1 Gas Chromatograph: a Carle Refinery Gas Analyzer, Model 196-Sx, equipped with a thermal conductivity detector, a ten port multi-functional gas sampling/switching valve, two additional switching valves and a palladium hydrogen transfer system.

3. APPARATUS Cont'd

3.2 Chromatographic Columns (Model 196-Sx)

Column 1	0.61 m x 3 mm OD(1/8 in.) - OPN/Porasil C, 150/180 µm (80/100) mesh
Column 2A	6.4 m x 3 mm OD(1/8 in.) - 27% BEEA on Chromasorb P, AW, 250/355 µm (45/60) mesh
Column 2B	3.4 m x 3 mm OD(1/8 in.) - OPN/Porasil C, 150/180 µm (80/100) mesh
Column 3	2.7 m x 3 mm OD(1/8 in.) - Porapak Q, 180-300 µm (50/80) mesh
Column 4	2.7 m x 3 mm OD(1/8 in.) - Molecular sieve 13X, 250/355 µm (45/60) mesh
Column 5	0.9 m x 3 mm OD(1/8 in.) - Molecular sieve 13X, 150/180 µm (80/100) mesh

NOTE 1: THE ABOVE INSTRUMENTATION IS AVAILABLE THROUGH TECHNICAL MARKETING ASSOCIATES, 6620 KITIMAT AVE., UNIT #6, MISSISSAUGA, ONTARIO. REPLACEMENT COLUMNS ARE NORMALLY PURCHASED FROM THE ABOVE.

NOTE 2: CARLE REFINERY GAS ANALYZERS ARE AVAILABLE WITH DIFFERENT COLUMNS, CONFIGURATIONS AND PEAK ELUTION ORDERS. IN ADDITION TO THE 196-SX THOSE BEING USED BY GULF ARE AS FOLLOWS:

MODEL 156-A: This is a first generation refinery gas analyzer. It consists of four columns used in conjunction with an eight-port multi-functional gas sampling/backflush-to-detector valve and two column switching valves. Unlike Model 196-Sx, the $C_5^{=}$ + C_6+ peak is eluted at the end of the analysis. Acetylene and propadiene are not resolved on this instrument.

MODEL 124-A: This instrument provides a rapid analysis of refinery gas liquids and LPG streams for carbon dioxide, air and C_1 -C_5 saturated and unsaturated hydrocarbons, with an initial backflush of C_5 unsaturates plus C_6+ saturates. A Carle Rotasphere Liquid Sampling System permits injection of pressurized liquid hydrocarbon samples. This system uses two columns and a six-port switching valve arranged in a "Series/Bypass" configuration. A Porapak column performs the separation of air (or nitrogen), methane, carbon dioxide, ethylene

3. APPARATUS Cont'd

NOTE 2: Cont'd
and ethane. A multiphase column provides separation of acetylene and C_3-C_5 hydrocarbons. Near baseline resolution of all C_3 and C_4 unsaturates is achieved, including butene-1 and isobutylene and 1,3-butadiene. A "flip-flop" valve/column configuration gives an initial C_5 unsaturate plus C_6 saturate backflush peak.

MODEL 126A: Natural gas or natural gas liquids are analyzed in this instrument. Either a gas sample valve or a Rotasphere High Pressure Liquid Sample valve is used to inject a sample onto a DC 200/500 on Gas Chrom RA column. After sample injection the air, carbon dioxide and C_1-C_5 hydrocarbons are separated and elute to the detector. As soon as the pentane elutes, the column is backflushed, regrouping the C_{6+} heavy ends as a composite peak.

3.2 Integrator: a computer system or a computing integrator comparable to the Autolab System I is recommended.

3.3 Recorder: 1 mV with a full scale response time of 1 second or less

3.4 Vacuum Pump: capable of evacuating to a pressure of 0.13 kPa

3.5 Carrier Gases: high purity helium and nitrogen

4. PROCEDURE

4.1 Adjust the instrument to the following conditions:

Helium	30 mL/min
Nitrogen	60 mL/min
Column Temperature	58°C
Hydrogen Transfer Temperature	585°C
Inlet ΔT Switch Position	Off

4. PROCEDURE Cont'd

4.2 Using normal chromatographic techniques, inject sample into the chromatograph using the gas sampling valve.

NOTE 3: SAMPLE INJECTION AS WELL AS VALVE SWITCHING ARE CONTROLLED BY COMPUTER OR INTEGRATOR CONTROLLED SOLENOIDS. THE TIMES OF THESE EVENTS HAVE BEEN PRE-DETERMINED BY THE MANUFACTURER BUT SHOULD BE PERIODICALLY UPDATED.

NOTE 4: TYPICAL EVENT AND FUNCTION TIMES AND COLUMN CONFIGURATIONS ARE REPORTED IN TABLE 1 AND FIGURE 1. A TYPICAL CHROMATOGRAM IS REPORTED IN FIGURE 2.

4.3 Integrate peak areas.

5. CALCULATION

5.1 Multiply peak areas by the appropriate response factors listed in Table 2.

$$\text{Component i, mass \%} = \frac{100\ Ai}{\Sigma A}$$

where Ai = response-corrected area of component i
ΣA = sum of response corrected areas

NOTE 5: TYPICAL MOLAR AND WEIGHT RESPONSE FACTORS ARE CONTAINED IN TABLE 2. THESE FACTORS MUST BE DETERMINED FOR EACH INSTRUMENT. IN SOME CASES, RESULTS EXPRESSED IN MOLE % MAY BE PREFERRED. CALCULATE THESE RESULTS SIMILARLY USING THE MOLAR RESPONSE FACTORS IN TABLE 2.

6. REPORT

Report the results as follows:

e.g. n-Butane (PCM 472) mass % = 4.32

7. PRECISION

7.1 Duplicate analysis should be considered suspect if they differ from the mean by more than 2% of the amount present.

8. TIME

Time required for an analysis is approximately 45 minutes.

9. APPENDICES

9.1 Table 1: Typical Time Functions

9.2 Figure 1: Valve Configuration

9.3 Figure 2: Typical Chromatogram

9.4 Table 2: Typical Response Factors for Carle Refinery Gas Analyzer

Research and Development Department

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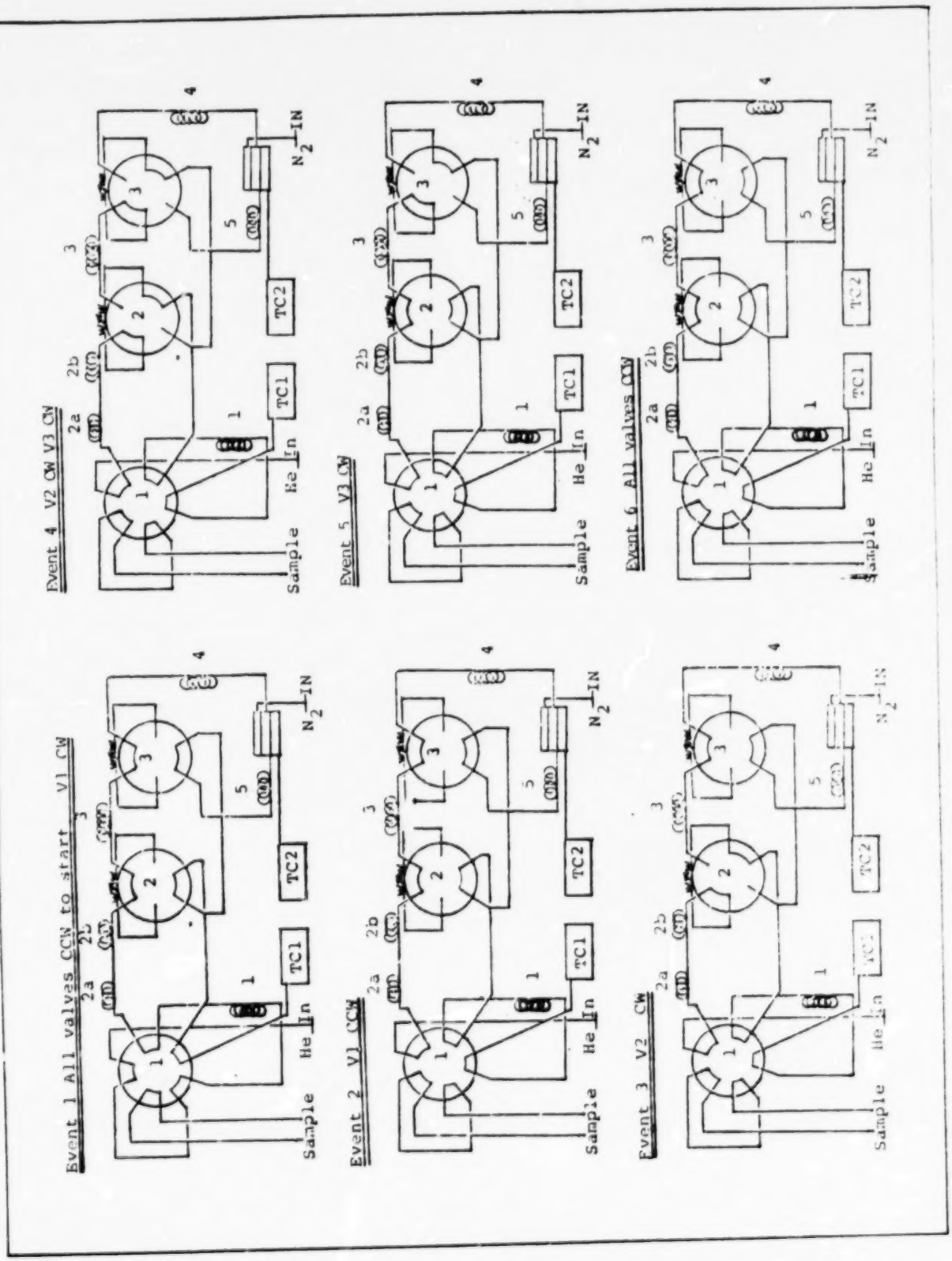
TABLE 1

SYSTEM I & CARLE TYPICAL TIME FUNCTIONS

ACTUATE	TIME (min/s)	FUNCTION	PEAKS ELUTING
MANUAL-RUN BUTTON	0/0	START - VI C.W., I.I. Set	
AUTO-T4 (Set 1)	2.6/156	- VI C.C.W.	
AUTO-T5 (Set 1)	3.0/180	- I.I. Reset	
AUTO-T3 (Set 1)	7.25/435	- V2 C.W.	$C_5^{=}$ + C_6^{+}, H_2
AUTO-T1 (Set 2)	7.26/436	- Automatic Change to Set 2	
AUTO-T6 (Set 1)	7.27/437	- V3 C.W.	C_3, $C_2^{=}$, C_3^{-}, H_2S iC_4, pronadiene nC_4, C_4^{-}-1, iC_4^{-}, tC_4^{-}-2 cC_4^{-}-2, 1,3 butadiene
AUTO-T3 (Set 2)	28.33/1700	- V2 C.C.W.	iC_5, nC_5
AUTO-T7 (Set 1)	34.91/2095	- V3 C.C.W.	CO_2, C_2^{-}, C_2
MANUAL - STANDBY	45.00/2700	- RUN RESET	O_2, N_2, C_1, CO

FIGURE 1: VALVE CONFIGURATION



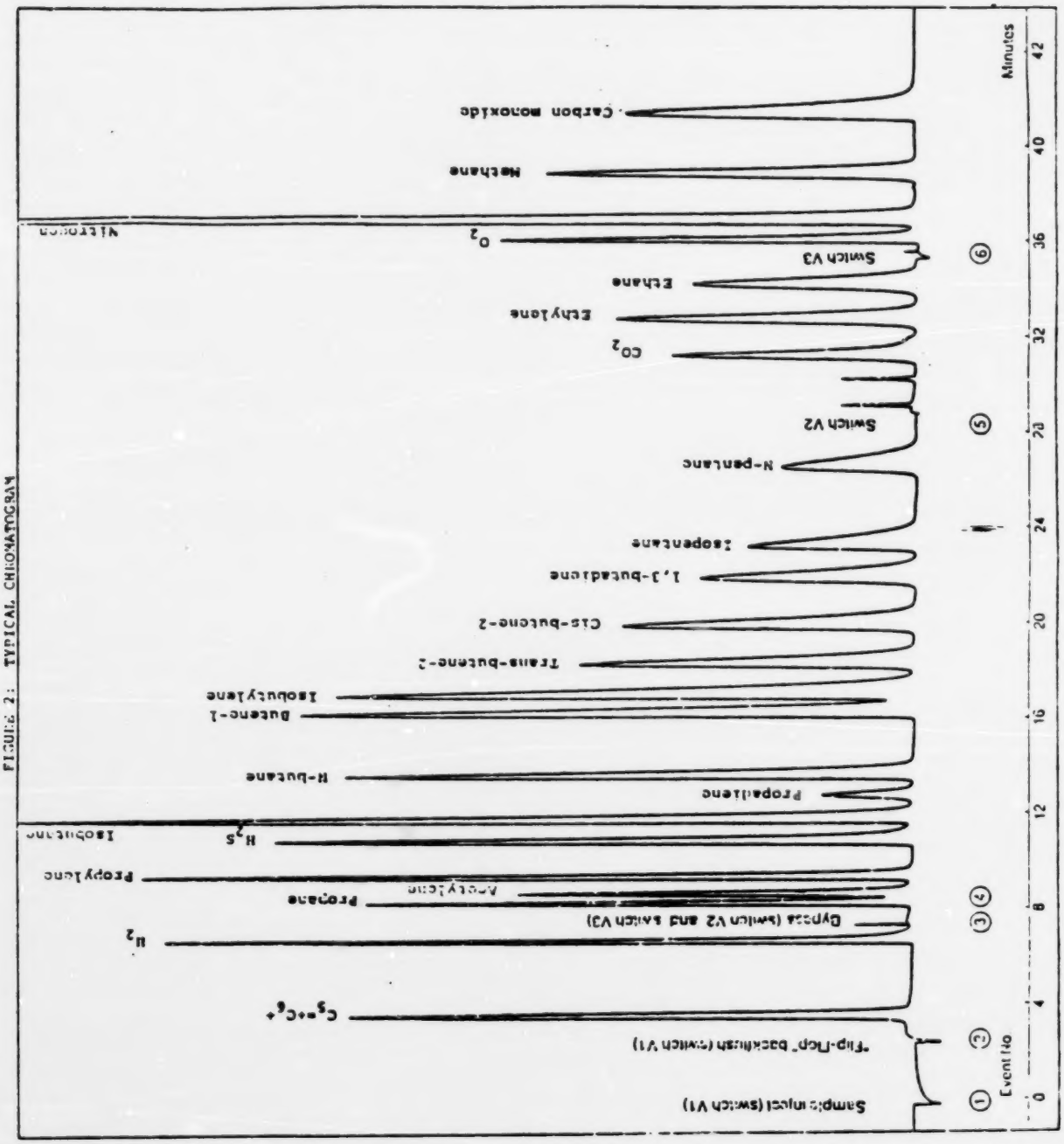


FIGURE 2: TYPICAL CHROMATOGRAM

TABLE 2

TYPICAL RESPONSE FACTORS FOR CARLE REFINERY GAS ANALYZER

Component	Mole Response	Weight Response
$C_5^{=} + C_6+$	0.770	0.7700
Hydrogen (low)	16.230	0.3246
(high)	17.170	0.3434
Propane	1.391	0.6120
Acetylene	1.867	0.4854
Propylene	1.448	0.6082
Hydrogen Sulphide	1.973	0.6708
Isobutane	1.220	0.7076
Propadiene	1.521	0.6084
Normal Butane	1.147	0.6653
Butene-1	1.185	0.6636
Iso-butene	1.206	0.6754
Trans butene-2	1.186	0.6644
Cis butene-2	1.179	0.6604
1,3 butadiene	1.259	0.6799
Isopentane	1.090	0.7848
Normal pentane	1.060	0.7632
Carbon Dioxide	1.939	0.8532
Ethylene	1.820	0.5096
Ethane	1.696	0.5088
Oxygen	2.440	0.7808
Nitrogen	2.276	0.6373
Methane	2.519	0.4030
Carbon Monoxide	2.228	0.6238

Union Carbide Molecular Sieves

molecular sieve catalyst data

CATALYST BASES LZ-M-5 AND LZ-M-8 POWDERS

DESCRIPTION

UNION CARBIDE LZ-M catalyst base powders are synthetic analogues of the zeolite modenite structure possessing a straight one-dimensional channel system characterized by a 6.7 × 7.0 Å pore opening. The LZ-M catalyst bases are currently available in two forms identified as LZ-M-5 powder and LZ-M-8 powder. LZ-M-5 is the non-acid, sodium cation form which can easily be modified by conventional ion exchange techniques[1] to produce a catalytically active material suitable for carbonium ion catalysis. LZ-M-8 is the low sodium, partially dealuminated, ammonium ion exchanged mordenite derived from LZ-M-5. Thermal treatment of LZ-M-8 drives off the ammonia creating the strong acid, catalytically active hydrogen form.

LZ-M-8 and modified forms of LZ-M-5 are recommended for various shape selective acid catalyzed reactions as well as typical hydrocarbon conversion reactions such as cracking, olefin alkylation, transalkylation and hydroisomerization of paraffins. LZ-M-8 can be used to selectively crack straight-chain paraffins in heavy petroleum fractions (e.g., catalytic dewaxing).

LZ-M zeolites have high acid stability and resist thermal degradation to over 900°C. The strong acidity of the hydrogen form of LZ-M-8 is demonstrated by the substantially higher n-butane cracking activity[2] value $k_A \cong 175$ compared to the stabilized HY catalyst LZ-Y-82 with $k_A \cong 30$. The acid activity of activated LZ-M-8 can be readily moderated by various levels of sodium ion exchange.

LZ-M-5 and LZ-M-8 powders are suitable for ion exchange, pore-filling or co-mulling with various noble metal or base metal solutions followed by forming into extrudates, tablets, etc. and calcination to produce the finished catalyst.

[1]Technical Bulletin F-09, "Ion Exchange and Metal Loading Procedures."
[2]Rastelli, H., Lok, B.M., Duisman, J.A., Earls, D.E. and Mullhaupt, J.T., The Canadian Journal of Chemical Engineering, 60, 44-49 (1982).

TYPICAL PHYSICAL PROPERTIES

	LZ-M-5	LZ-M-8
Surface Area, m^2/g	420	480
Oxygen Capacity (−183°C @100 Torr), wt. %	16.5	18.2
L.O.I. at 1000°C	13.1	16.7

TYPICAL CHEMICAL PROPERTIES (WT. % ANHYDROUS)

	LZ-M-5	LZ-M-8
SiO_2	78.7	86.1
Al_2O_3	12.5	8.6
Na_2O	7.33	0.05
$(NH_4)_2O$	0.0	4.4
SiO_2/Al_2O_3 (molar ratio)	10.7	17.0
Na_2O/Al_2O_3 (molar ratio)	0.96	0.01

AVAILABILITY

CATALYST BASES LZ-M-5 and LZ-M-8 are available in quantities up to 200 pounds per year for your product development. Research quantities, of one-half pound, are available for your experimental use and larger quantities, up to 200 pounds, for your pilot plant applications.

Shipments are made in tightly sealed non-returnable steel cans or drums. Research quantities are shipped by parcel post; pilot plant quantities, by truck unless otherwise specified by the buyer. Prices are F.O.B. seller's plant at Chickasaw, Alabama; terms are net 30 days.

TASK 5 - FLAMMABILITY CALCULATIONS

Ratio HC*/N_2O	Percent CH_4	Percent C_3H_6	Percent N_2O	% CH_4 in N_2O	% C_3H_6 in N_2O
1:1	50	-	50	50	-
4:1	80	-	20	80	-
10:1	90.9	-	9.1	90.9	-
1:1	45	5	50	47.4	9.1
4:1	71.9	8.1	20	78.2	28.8
10:1	81.8	9.1	9.1	90.0	50.0

		CH_4	C_3H_6
Flammability Limits**:	Lower	2.2%	1.45%
	Upper	36.6%	28.8%

* HC = Total Hydrocarbon

** Reference: Limits of Flammability of Gases and Vapours
Bulletin 503 - U.S. Bureau of Mines